

REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-01-

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1. REPORT DATE (DD-MM-YYYY) 30-09-01		2. REPORT TYPE Final Report		5. FUNDING NUMBERS 5/15/98-5/14/01	
4. TITLE AND SUBTITLE Physical and Chemical Processes in Flames				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER F49620-98-1-0075	
				5c. PROGRAM ELEMENT NUMBER 61102F	
6. AUTHOR(S) Chung K. Law				5d. PROJECT NUMBER 2308	
				5e. TASK NUMBER BX	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Mechanical & Aerospace Engineering Princeton University Princeton, NJ 08544				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NA 801 Randolph Street Room 732 Arlington VA 22203-1977					
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The objectives of the program were two fold, namely (1) to identify the controlling chemistry of aeropropulsion fuels and develop detailed and reduced mechanisms describing their oxidative reaction pathways and rates, and (2) to understand and quantify the unstable modes of combustion and their influence on flame extinction. Concerning Objective 1, laminar burning velocities of C ₁ to C ₈ alkanes with air, and blends of butane, ethylene and benzene with air, were experimentally measured. These results were used, together with other chemical kinetic information towards the development of a comprehensive C ₈ -mechanism. A mathematical theory based on computational singular perturbation was formulated, allowing for the systematic reduction of detailed reaction mechanism to simpler ones without loss of the comprehensiveness of the kinetic description. Concerning Objective 2, the steady and pulsating propagation of flames were analytically and computationally studied, at atmospheric and elevated pressures. Results showed that the onset of pulsation facilitates flame extinction, that positive and negative stretch respectively promote and retard its onset, that radiative loss promotes flame front instability and extinction, and that there is strong coupling between flame front stability and the intrinsic chemical chain mechanisms. These results are expected to be useful to the general interests of AFOSR in the fundamental and practical issues of flame dynamics and chemical kinetics, turbulent combustion, radiative heat transfer, flame extinction, stabilization, flammability, and supersonic combustion.					
15. SUBJECT TERMS Hydrocarbon oxidation chemistry, burning velocities, hydrogen combustion, computational singular perturbation, pulsating instability, extinction, radiation, high pressure combustion					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	UL	22	Julian M. Tishkoff
				19b. TELEPHONE NUMBER (include area code) (703) 696-8478	

20011126 089

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Final Report

Grant Number: F49620-98-1-0075

PHYSICAL AND CHEMICAL PROCESSES IN FLAMES

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SUMMARY/OVERVIEW

The objectives of the program were two fold, namely (1) to identify the controlling chemistry of aeropropulsion fuels and develop detailed and reduced mechanisms describing their oxidative reaction pathways and rates, and (2) to understand and quantify the unstable modes of combustion and their influence on flame extinction. Concerning Objective 1, laminar burning velocities of C_1 to C_8 alkanes with air, and blends of butane, ethylene and benzene with air, were experimentally measured. These results were used, together with other chemical kinetic information towards the development of a comprehensive C_3 -mechanism. A mathematical theory based on computational singular perturbation was formulated, allowing for the systematic reduction of detailed reaction mechanism to simpler ones without loss of the comprehensiveness of the kinetic description. Concerning Objective 2, the steady and pulsating propagation of flames were analytically and computationally studied, at atmospheric and elevated pressures. Results showed that the onset of pulsation facilitates flame extinction, that positive and negative stretch respectively promote and retard its onset, that radiative loss promotes flame front instability and extinction, and that there is strong coupling between flame front stability and the intrinsic chemical chain mechanisms. These results are expected to be useful to the general interests of AFOSR in the fundamental and practical issues of flame dynamics and chemical kinetics, turbulent combustion, radiative heat transfer, flame extinction, stabilization, flammability, and supersonic combustion.

ACCOMPLISHMENT

Highlights of the accomplishments can be found in the annual reports submitted to the program director, as well as the journal and conference papers that have appeared in print. Thus only a brief summary of these works is mentioned in the following.

Development of Comprehensive Kinetic Mechanisms for Hydrocarbon Oxidation

Recognizing the lack of a comprehensive chemical kinetic mechanism for aeropropulsion fuels in general, and the significantly reduced residence time and hence heightened performance sensitivity to chemical kinetics in supersonic combustion in particular, an experimental-computational effort was initiated for the development of such a mechanism for hydrocarbon fuels up to C_8 . The basic requirements for this mechanism include: (a) fundamental input of thermochemistry and elementary reaction kinetics; and (b) predictive capability of the wide spectrum of combustion phenomena, from the response of homogeneous systems such as shock tube and auto-ignition delays, to the ignition, steady burning, and extinction of premixed and diffusion flames for which diffusive transport is present, and ultimately to the characteristics of pollutant formation. The reaction mechanism should also be applicable to a wide variety of hydrocarbon fuels and should incorporate any pressure effects on the combustion responses. To achieve this goal, experiments were conducted to acquire fundamental combustion data such as the laminar burning velocities and the extinction of stretched premixed and diffusion flames, while *ab initio* quantum mechanical calculations were also performed to determine the rate coefficients. To bring the fundamental understanding of reaction kinetics to a predictive model, systematic optimization of the reaction rate parameters within their uncertainties was performed, and the optimized model validated against an even wider range of combustion data. Lastly, attempts were initiated to reduce the detailed reaction mechanisms to smaller mechanisms that are still quantitatively predictive but are sufficiently simple for implementation in large-scale modeling.

During this period of funding, significant progress was made on the combustion kinetics of low molecular-weight fuels, including acetylene, ethylene, propyne, allene, propene, propane, and butadiene. The reaction kinetics of these fuels constitutes a critical subset of a comprehensive mechanism of aeropropulsion fuels. In addition to the study of small hydrocarbons and recognizing the lack of reliable, fundamental combustion data for alkane and alkene fuels in general, a comprehensive experimental study on the laminar burning velocities of

C₁ to C₈ hydrocarbons, as well as some fuel blends, was also conducted. These data are critical for the present and future tasks of mechanism development.

Theoretically, high-level *ab initio* calculations were performed for a number of reaction systems pertinent to C₂ and C₃ combustion. The reaction rate constants were determined by the Rice-Ramsperger-Kassel-Marcus (RRKM) theory. Numerically, sensitivity analysis was conducted using detailed reaction mechanisms, which were validated against a variety of experimental data, including fuel pyrolysis and oxidation in shock tubes, laminar burning velocities, and detailed species time and spatial profiles in static reactors or in combusting flows.

Progress made in this endeavor is reported in the following.

1. Combustion Chemistry of Propane: A Case Study of Reaction Mechanism Optimization

Detailed reaction mechanisms describing hydrocarbon combustion have hierarchical structures with H₂ and CO chemistry at the base, supplemented by necessary reaction channels of larger chemical species. While this strategy provides rational organization of combustion chemistry, it is unknown whether parameter sets derived by optimizing smaller-hydrocarbon chemistry are secure foundations for extension to larger-hydrocarbon oxidation models. This question was addressed in the present work by combining the newly optimized GRI-Mech 3.0 for methane and ethane combustion with the C₃H_x chemistry developed by us previously. Model predictions were compared against methane, ethylene, ethane, propyne, allene, propene, propane laminar burning velocities and shock tube ignition delay data. It was found from extensive sensitivity testing that the coupling between the C₃H_x chemistry and the C₁-C₂ kinetic subset was much stronger than anticipated. The C₃H_x combustion data could not be satisfactorily modeled using the C₁-C₂ kinetic subset without re-optimizing some of the C₃ kinetic parameters. These parameters have stronger influences on C₃H_x combustion than the C₃ parameters. Parameter optimization analogous to the GRI-Mech 3.0 optimization was carried out using essentially the same methods as were used in the development of C₁-C₂ kinetic subset, including 21 optimization targets, of which 9 were ignition delays and 12 were atmospheric pressure laminar burning velocities. A reasonable match to the whole target set could be obtained, without deteriorating the agreement between experiment and calculation for the methane and ethane combustion data, by re-optimizing 9 parameters from the C₁-C₂ kinetic subset.

The implication of this study is significant in that any reaction mechanisms proposed previously and many more to come represent just individual points within the uncertainty space

of a given kinetic set. Maximizing the likelihood that a kinetic model can predict a combustion property beyond the regime within which the model is validated can only be achieved by comprehensive optimization. In this way the size of the uncertainty space is reduced only to an extent as being inconsequential to the combustion of a given set of target fuels. The second implication of the study is that kinetic model optimization in a multi-parameter, -target, and -fuel space is entirely possible as will be pursued in our research program. Through this study, we also developed a tentatively optimized combustion model, which predicts very well a wide variety of C_1 - C_3 fuel combustion.

2. Propene Pyrolysis and Oxidation Kinetics in Flow Reactor and Laminar Flames

The pyrolysis and oxidation of propene were studied experimentally in an atmospheric flow reactor. Species profiles were obtained in the intermediate to high temperature range (~1200 K) for lean, stoichiometric, rich, and pyrolytic conditions. Laminar burning velocities of propene/air mixtures were also determined over an extensive range of equivalence ratios, at room temperature and atmospheric pressure, using the counterflow twin flame configuration. A detailed chemical kinetic model consisting of 465 reactions and 71 species was used to describe the high temperature kinetics of propene, propyne, allene, and propane. It was shown that the kinetic model could accurately predict a wide range of combustion data for these fuels, including laminar burning velocities, speciation in flow reactors, and ignition in shock tubes. Notable uncertainties in the reaction kinetics of these fuels are identified and discussed.

3. RRKM, Flow Reactor, and Detailed Kinetic Modeling Study of Propyne Pyrolysis and Oxidation

The oxidation of propyne was studied experimentally in an atmospheric flow reactor and in laminar premixed flames. Species profiles were obtained for propyne oxidation experiments conducted in the Princeton Turbulent Flow Reactor in the intermediate to high temperature range (~1170 K) for lean, stoichiometric, and rich conditions. A detailed chemical kinetic model of high-temperature propyne oxidation, consisting of 437 reactions and 69 species, was developed. It was shown that this kinetic model predicts reasonably well the flow-reactor and flame-speed data determined in the present study, and the shock-tube ignition data available in the literature. The remaining uncertainties in the reaction kinetics of propyne oxidation were discussed and an important part of the reaction kinetics was examined.

The pressure-dependent rate coefficients for several reactions relevant to propyne pyrolysis were determined with *ab initio* quantum mechanical calculations and Rice-Ramsperger-Kassel-Marcus (RRKM) analyses. These include the mutual isomerization of propyne and allene, the chemically activated reactions of propyne and allene with the H atom and of acetylene with methyl on the C_3H_5 potential energy surfaces. Propyne pyrolysis was also experimentally studied in a flow reactor at 1210 K and 1 atm. A detailed reaction mechanism, employing the current RRKM rate coefficients, was shown to accurately predict the experimental acetylene and methane profiles determined in the flow reactor and literature shock-tube data of propyne and allene pyrolysis up to 1500 K.

4. Quantum Mechanical and Kinetic Modeling Studies of the Initiation Reactions in Acetylene Oxidation in Shock Tube

The reaction kinetics of acetylene underlies all hydrocarbon combustion kinetics. Acetylene oxidation has been extensively studied in shock tubes. A large amount of data exists, which can be used to verify the acetylene subset of the detailed reaction mechanism for aeropropulsion fuels. However, validation of this mechanism subset has been hampered by a long-standing and unresolved issue in acetylene oxidation, namely the nature of the oxidation initiation processes. For this reason, the reaction between acetylene and molecular oxygen was analyzed using quantum mechanical calculations and kinetic modeling of acetylene oxidation in shock tubes. Calculations at the G2(B3LYP) level of theory showed that the direct attack of molecular oxygen on the p bond in acetylene has a larger energy barrier than acetylene-vinylidene isomerization, such that this isomerization followed by the reaction of vinylidene with molecular oxygen is the energetically favorable initiation reaction of acetylene oxidation. It is further shown that detailed kinetic models of acetylene oxidation including this initiation process predict well the experimental shock tube ignition delay data. Through this study, it is the first time that a carbene species is proposed as the major player in the initiation process of unsaturated hydrocarbon oxidation. It remains to be seen whether such a mechanism is generally applicable to the oxidation of other unsaturated hydrocarbons as well.

5. Experiments and Detailed Kinetic Modeling of 1,3-Butadiene Oxidation at High Temperatures

The oxidation kinetics of 1,3-butadiene ($1,3-C_4H_6$) is of considerable importance to the hierarchical development of the kinetic mechanisms of long-chain aliphatics and aromatics

combustion. Previously a comprehensive kinetic model of acetylene, ethylene, allene, propyne, propene, and propane combustion was developed. This model can predict a wide variety of combustion responses from ignition and laminar flame propagation to the overall and detailed structures of fuel oxidation and combustion. This previous model was extended to include the kinetics of 1,3-butadiene pyrolysis and oxidation.

Specifically, the high-temperature kinetics of 1,3-butadiene oxidation was examined with detailed kinetic modeling. To facilitate model validation, flow reactor experiments were carried out for 1,3-butadiene pyrolysis and oxidation over the temperature range 1035-1185 K and at atmospheric pressure, extending similar experiments found in the literature to a wider range of equivalence ratios and temperatures. The kinetic model was compiled on the basis of an extensive review of literature data. The reaction pathways and rate constants of several key reactions were examined closely by a detailed analysis of previous experimental results, by thermochemical considerations, and by Rice-Ramsperger-Kassel-Marcus (RRKM) calculations. Notably these reactions include the attack of the H and O atoms on 1,3-butadiene. The accuracy of the rate constants associated with these reactions proves to be critical to the overall kinetics of 1,3-butadiene pyrolysis and oxidation.

The kinetic model was critically validated against a total of 15 sets of experimental data including species profiles during 1,3-butadiene pyrolysis and oxidation in flow reactors and shock tubes, and 1,3-butadiene flames. It was shown that the kinetic model compiled in this study is capable to closely predict a wide range of high-temperature oxidation and combustion responses.

The analysis of individual reactions and the reaction pathway based on the current kinetic model revealed a viewpoint of 1,3-butadiene kinetics significantly different from previous studies. Three parallel pathways were identified to be relevant to 1,3-butadiene oxidation, with the chemically activated reaction of H and 1,3-butadiene to produce ethylene and the vinyl radical being the most important channel over all experimental conditions. Extensive sensitivity analyses were performed; and the remaining uncertainty of the butadiene chemistry was discussed.

6. Determination of and Fuel Structure Effects on Laminar Burning Velocities of C₁ to C₈ Hydrocarbons

Laminar burning velocities determined by using the counterflow twin flame configuration were compared for various C_1 to C_8 hydrocarbons, including alkanes, alkenes, alkynes, aromatics, and alcohols. The data were compared over an extensive range of equivalence ratios at room temperature and atmospheric pressure. The comparison showed that the laminar burning velocities of normal alkanes are close throughout the entire range of equivalence ratios studied, except for methane whose flame speeds are consistently lower. The more unsaturated the molecule the higher the burning velocity for fuels having the same carbon number in the order of alkanes < alkenes < alkynes. Methyl substitution for hydrogen or branching reduces the flame speeds for both alkanes and alkenes. The burning velocities of large saturated cyclic species (cyclohexane and cyclopentane) are close to those of their normal alkane analogs.

7. Laminar burning Velocities of Ethylene/*n*-Butane/Air Mixtures

The objectives of the present study were: (a) to extend previous study involving single fuels to fuel blends, and (b) to experimentally determine the burning velocities by using Digital Particle Image Velocimetry (DPIV).

Regarding the first objective, it is noted that since nearly all practical fuels are multi-component, it is important to develop theoretical and semi-empirical capabilities to predict the flame speeds of fuel mixtures. Furthermore, existing reaction models of hydrocarbon combustion were mostly developed based on results from single fuels and as such have not been adequately verified for fuel mixtures. Finally, it is also of interest to develop semi-empirical mixing rules.

Mixtures of ethylene and *n*-butane were selected for study because ethylene is an important intermediate in hydrocarbon oxidation while *n*-butane is a representative *n*-alkane. The experimental data of the laminar burning velocities of ethylene/air and *n*-butane/air mixtures were found to compare well with the calculated values obtained by using the kinetics model developed under the present program. Using this kinetics model, further calculations were performed for mixtures of ethylene and *n*-butane in the ratios of 2:1, 1:1, and 1:2. As is reasonable to expect, the burning velocities of the fuel mixtures are bounded by those of ethylene/air and *n*-butane/air. However, results for the mixtures seem to be weighted towards the *n*-butane values. The same biasing is also exhibited for the calculated adiabatic flame temperatures, indicating that the flame temperature instead of kinetic coupling could have the dominant influence on the burning velocity. The biasing could simply be a consequence of how

the composition of mixture is defined. The present mixing ratio is the conventional one, based on the molar ratios. There are, however, other definitions that could be more relevant physically. This aspect is being studied.

Studies on Chemistry-Related Problems

8. Effect of Inelastic Collision on Binary Diffusion Coefficients of Free Radicals

Diffusion is a key factor in chemically reacting flows in which the propagation rate of a flame is determined by diffusion as well as chemical reaction and heat release. It is known that the sensitivity of flame propagation to the H-atom diffusion coefficient is as large as that of the free-radical chain branching reaction $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$. Despite the recent progress in the description of H-atom diffusion coefficient, the molecular theory of H-atom diffusion remains to be that of Chapman-Enskog, in which elastic collision is assumed. On the other hand, it is known that collision of the H atom with notable combustion species including H_2 , CO, CO_2 , O_2 , C_2H_2 , and C_2H_4 is inelastic at combustion temperatures. At very high temperatures, say, 2500 K, nearly a quarter of collision encounter between the H atom and N_2 is inelastic. This inelastic collision can be best described by the formation of a transient chemical bond, whose binding energy is of the order of 10^3 times larger than the well depth of a typical Lennard-Jones potential. In this work, we examined the influence of inelastic collision on diffusion coefficients. Our aim was to obtain an order-of-magnitude estimate for this influence, and compare it to the influence of reaction rate parameters. In this way the uncertainty resulting from the diffusion coefficients could be assessed.

Diffusion coefficient was examined using molecular dynamics simulation and the Green-Kubo formula, with pair interaction potential energies corresponding to collision with and without the elastic assumption. It was found that inelastic collision significantly increases the diffusion coefficients of free radical species at temperatures relevant to fuel combustion. Inelastic collision with a potential energy curve representative of molecule-radical interaction may cause the diffusion coefficient to increase by as much as 50% at 1500 K. This finding suggests that a molecular theory beyond the Chapman-Enskog equation is needed to describe accurately free-radical diffusion in laminar flames.

9. Theory of Complex Computational Singular Perturbation

The method of Computational Singular Perturbation (CSP) for the analysis and reduction of detailed chemical mechanisms was extended to the complex eigensystem. Results showed that the time scales of chemical species change dramatically and non-monotonically, and that oscillatory modes appear frequently in large chemical reaction mechanisms. The present method was then employed to generate reduced mechanisms for hydrogen/air and methane/air oxidation.

Using the hydrogen/air system as an example, it was found that the number of complex modes increases with decreasing residence time and hence increasing chemical sensitivity, and that the longer the residence time the more the number of steady-state species and hence the smaller the mechanism. The validity of these reduced mechanisms was evaluated based on the responses of the perfectly stirred reactors and the one-dimensional planar propagating premixed flames. Comparison between the reduced and detailed chemistries over a wide range of pressures and equivalence ratios showed good agreement on the flame speed, temperature and structure.

10. Structure and Sooting Limits of Diffusion Flames from 1 to 5 Atmospheres

Previous studies on the structure and soot formation of atmospheric, non-sooting and near-sooting counterflow ethylene diffusion flames showed that the experimental soot volume fractions and laser scattering signals can be satisfactorily predicted by a detailed kinetic model of soot formation. By further extending the study to include the influence of pressure and fuel dilution on the critical sooting strain rates, it was identified that, when the flame temperature is held constant, the density-weighted strain rate at the sooting limit can be correlated with the system pressure, p , and fuel mole fraction, X_F , according to $\rho_o K_p \sim p X_F^{0.5}$, where ρ_o is the mass density of the cold oxidizer gas mixture, and K_p the local strain rate at the sooting limit. Hence, a plot of $\rho_o K_p$ versus $p X_F^{0.5}$ defines the sooting boundary in that the region above the limit is non-sooting, and that below it is sooting. It was further shown that such a correlation could be understood by plotting $p X_F^{0.5}$ versus the peak acetylene partial pressure, which again exhibits a linear dependence. Hence a linear relationship exists between the sooting limit, $\rho_o K_p$, and the partial pressure of acetylene, implying that a larger acetylene partial pressure requires stronger straining to prevent soot formation.

The sooting limit correlation identified highlights the practical significance of such a correlation, in that it provides an unambiguous means to predict whether a flame environment

with given strain rate, pressure, and fuel mole fraction would result in a local sooting condition in a complex flame environment such as the turbulent diffusion flame. In addition, the simplicity of the correlation indicates its fundamental importance, which is yet to be fully understood through kinetic modeling studies.

The present work extended the study to methane and propane flames. The temperature and major species concentration profiles were measured with spontaneous Raman scattering, and computationally simulated with detailed kinetics and transport. Good agreement was found between the experimental data and the computational simulation, hence providing benchmark data for further studies. It was also shown that the previously developed global and local sooting limit correlations are again applicable, respectively relating the density-weighted strain rate at the sooting limit with the global parameters of the system pressure and fuel mole fraction in the fuel stream, and with the local flame parameter of the peak acetylene partial pressure. This again demonstrated the importance of acetylene as a crucial intermediate in soot formation in flames. In addition, the local correlations for the propane and ethylene flames collapse into a single relation. The fact that the correlation for the methane flames is different from those of propane and ethylene is not unexpected considering the significantly different kinetic features of methane from those of other fuels, particularly in terms of the detailed reaction kinetics of PAH and soot formation from methane, which is yet to be fully understood.

Unsteady Flame Dynamics

11. Steady and Pulsating Propagation of Rich Hydrogen/Air Flames at Atmospheric and Elevated Pressures

Previous computational simulation of atmospheric one-dimensional planar hydrogen/air flames with detailed chemistry and transport showed that pulsating instability develops as the rich flammability limit is approached. Specifically, for $\phi=7.3$, the maximum flame temperature and hence flame propagation remain steady. However, the propagation becomes oscillatory at $\phi=7.4$, changes to period doubling at $\phi=7.6$, and extinguishes at $\phi=7.8$. Since the steady-state extinction turning point occurs at $\phi=10.22$, the result showed that oscillation reduces the flammability limit defined for the steady flame.

The present study extended the previous investigation to include effects of elevated ambient pressure, for pressures ranging from 1 to 20 atmospheres, with emphasis on the

influence of chain-mechanisms in H_2/O_2 oxidation. For steady burning, with increasing pressure, the burning rate first increases, then decreases, and then increases again, thereby resulting in the occurrence of a maximum burning rate and a minimum burning rate. It was further found that the states of maximum and minimum burning rates largely correspond to those of the crossover temperature. Sensitivity analysis then demonstrated that the first regime is dominated by the $\text{H}+\text{O}_2$, $\text{O}+\text{H}_2$, and $\text{OH}+\text{H}_2$ fast-branching sequence, the second regime is significantly influenced by the $\text{H}+\text{O}_2+\text{M}$ terminating reaction, and the third regime is dominated by the slow-branching HO_2 and H_2O_2 chemistry. It is significant to recognize that the response of the burning rate, which is expected to be fundamentally affected by diffusion, follows that of the explosion chemistry of the homogeneous system.

Further calculations were performed for the states of steady extinction, the onset of pulsation, and the extinction of the pulsating flame. It was again observed that pulsating extinction occurs at lower concentrations than those of the steady flames, indicating a narrowing of the flammability limit when considering flame unsteadiness. Furthermore, the states for the onset of pulsation are very close to those of the maximum burning rate, which implies that the onset of pulsation is also controlled by the crossover temperature. The cause for this very close coincidence has yet to be identified, although it must be somehow related to the slowing down of the reaction rate by the $\text{H}+\text{O}_2+\text{M}$ reaction, beyond the maximum burning state, and thereby the increase in the effective activation energy. This in turn favors the Sivashinsky criterion $\text{Ze}(\text{Le}-1)>11$ for the onset of pulsating instability, where Ze is the Zel'dovich number and Le the Lewis number.

The study also found that a mixture that is pulsatingly extinguishable, and hence nonflammable, can assume a steady burning mode at higher pressures. This is caused by the reduction in the effective activation energy for the weakly branching reactions that are dominant under high pressures.

12. Pulsation and Flammability Limits of Lean Heptane/Air Flames

The unsteady propagation of lean heptane/air planar flames in the doubly infinite domain was computationally simulated with detailed chemistry and transport, and with and without radiative heat loss. For the adiabatic situation, thermal-diffusive pulsating instability, promoted for large values of the Lewis and Zeldovich numbers, was observed to develop when the mixture becomes sufficiently lean. With subsequent progressive reduction in the equivalence ratio, ϕ , the

mode of pulsation changes from that of monochromatic, to period doubling, and to bursting characterized by bursts of high burning intensity separated by long period of dormancy. The flame nevertheless does not extinguish. This behavior is similar to that of the rich hydrogen/air flame studied previously. However, when heat loss is considered, the onset of pulsation is facilitated, although the regime in ϕ for sustained pulsating propagation is extremely narrow, and extinction occurs readily when the amplitude of the flame temperature oscillation becomes large enough to extinguish the flame during the negative phase of excursion. The abruptness of transition to extinction is quite different from that of the rich hydrogen/air flame. The pulsating extinction occurs at a larger ϕ ($\phi=0.5063$) than steady extinction ($\phi=0.4762$), again implying that the flame extinguishes in the pulsating instead of the steadily propagating mode, and that the flammability limit is accordingly narrowed. It was further demonstrated that the states for the onset of adiabatic and non-adiabatic pulsations can be accurately estimated by respectively using the criterion of Sivashinsky and of Joulin and Clavin, provided that the Lewis number used is the global one, extracted from the response of stretched flames. This therefore demonstrates that the Lewis number is a property of the flame instead of the unburned mixture alone. It is also suggested that the lean flammability limits of mixtures of large hydrocarbons and air can be estimated by using the criterion of Joulin and Clavin.

13. Effects of Stretch on Flame Pulsation

Effects of stretch on the pulsating instability of premixed flames were investigated via the negatively stretched inwardly propagating spherical flame (IPF) and the positively stretched counterflow flame (CFF). Computational and asymptotic analysis results showed that pulsating instability is suppressed by the former and promoted by the latter. In particular, it was shown that for a given rich hydrogen/air mixture whose one dimensional, freely propagating flame is pulsatingly unstable, the IPF initially propagates at the laminar burning velocity when the flame radius is large. Oscillation subsequently develops, and is then amplified, damped, and eventually suppressed as the flame propagates inward and the magnitude of stretch increases. For the positively stretched rich hydrogen/air CFF, oscillation is initiated at an equivalence ratio much smaller than the one-dimensional rich threshold. Furthermore, the critical strain rate leading to pulsation is smaller than the corresponding static extinction limit, implying that the flame extinguishes in the pulsating instead of the steadily propagating mode such that the flammable range is accordingly narrowed. In addition, it is seen that the pulsating flames are quasi-steady in

nature in that the period of oscillation is larger than the characteristic flame time. As such, the unsteady flame cannot recover once the instantaneous flame temperature is reduced below the corresponding steady-state extinction temperature.

The computationally determined pulsation limits using realistic chemistry and transport were also found to agree well with the asymptotic results based on simplified chemistry and transport, provided that the global activation energies and Lewis numbers are appropriately extracted from laminar flame responses.

14. Oscillatory Extinction of Diffusion Flames

The transient behavior of spherical diffusion flames was computationally studied in both the high-velocity and radiation-induced limit of the isola response of flame extinction. Oscillatory instability was observed near both steady-state extinction limits, with the oscillation amplitude growing until it becomes large enough to extinguish the flame. For the hydrogen and methane flames studied, oscillation always leads to extinction, although the characteristics of oscillation are qualitatively different. Specifically, the methane flame exhibits large amplitude temperature fluctuations at a frequency of about 0.35 Hz, while the hydrogen flame has small amplitude fluctuation with a frequency of about 60 Hz. The oscillations in the methane flame appear to be characteristic of those studied based on the diffusion flame structure, while those of hydrogen flames are reminiscent of those observed in rich hydrogen/air premixed flames.

15. Radiation Induced Flamefront Instability

Unsteady propagation and instability of radiative stretched premixed flames at Lewis numbers close to unity were numerically investigated using helium-diluted counterflow methane flames. The objective was to understand the stability of the three near-limit and sub-limit multiple flame regimes, namely the near stagnation flame, the weak flame, and the distant flame. It was shown that both the near-limit and sub-limit near-stagnation flames are stable close to the flammability limit, and that a new mode of oscillation instability exists at equivalence ratios sufficiently larger than that at the flammability limit. In addition, stability of the weak and the distant flames was demonstrated, while unsteady mutual transitions between the near-stagnation flame and the distant flame, and the jump from the weak flame to the normal flame, were found. A comparison of the present prediction with the microgravity experimental observation showed qualitative agreement on the oscillation frequency and the regime for the occurrence of

oscillation. Calculations for Lewis numbers larger and smaller than unity showed that the radiation induced instability is a physically intrinsic phenomenon for radiative stretched premixed flame.

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11. "Pulsating instability in near-limit propagation of rich hydrogen/air flames," by E.W. Christiansen, C.J. Sung, and C.K. Law, *Twenty-seventh Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, pp. 555-562 (1998).
12. "Radiation induced instability of stretched premixed flames," Y. Ju, C. K. Law, K. Maruta, and T. Niioka, *Proceedings of the Combustion Institute*, Vol. 28, pp. 1891-1900 (2000).
13. "Structure, aerodynamics, and geometry of premixed flamelets," by C.K. Law and C.J. Sung, *Progress in Energy and Combustion Science*, Vol. 26, pp. 459-505 (2000).
14. "Structural sensitivity, response, and extinction of diffusion and premixed flames in oscillating counterflow," by C. J. Sung and C. K. Law, *Combustion and Flame*, Vol.123, pp. 375-388 (2000).
15. "On curvature-affected pulsating instability in inwardly-propagating spherical flames," by C. J. Sung, C. J. Sun, and C. K. Law, *Combustion Science and Technology Communications*, Vol.1, pp. 7-10 (2000).
16. "The role of pulsating instability and global Lewis number on the flammability limit of lean heptane/air flames," by E. W. Christiansen, C. K. Law, and C. J. Sung, *Proceedings of the Combustion Institute*, Vol. 28, pp. 807-814 (2000).
17. "Steady and pulsating propagation and extinction of rich hydrogen/air flames at elevated pressures," by E. W. Christiansen, C. J. Sung, and C. K. Law, *Combustion and Flame*, Vol. 124, pp. 35-49 (2001).

PREPRINTS AND REPORTS

1. "Structural Sensitivity, Response and Extinction of Unsteady Counterflow Flames," by C. J. Sung and C. K. Law, AIAA Paper No. 98-0555, 36th Aerospace Sciences Meeting, Reno, NV, January 12-15, 1998.
2. "Influence of Chemical Kinetics in the Self-Ignition of Nonpremixed Supersonic Hydrogen-Air Flows," by C. J. Sung, J. G. Li, G. Yu, and C. K. Law, AIAA Paper No. 98-0722, 36th Aerospace Sciences Meeting, Reno, NV, January 12-15, 1998.
3. "Steady and Pulsating Propagation and Extinction of Rich Hydrogen/Air Flames at Elevated Pressures," by E. W. Christiansen, C. J. Sung, and C. K. Law, AIAA Paper No. 99-0205, 37th Aerospace Sciences Meeting, Reno, NV, January 11-14, 1999.
4. "Soot Formation in Fluctuating Flows," by D. L. Zhu, C. J. Sung, and C. K. Law, AIAA Paper No. 99-0451, 37th Aerospace Sciences Meeting, Reno, NV, January 11-14, 1999.
5. "The Pyrolysis and Oxidation of Propene in Flow Reactor," by S. G. Davis, C. K. Law, and H. Wang, Paper No. 2, Meeting of the Joint U.S. Section of the Combustion Institute, Washington, DC, March 15-17, 1999.
6. "A Theoretical Study of the Chemically Activated Reactions on the C_3H_5 Potential Energy Surface," by S. G. Davis, C. K. Law and H. Wang, Paper No. 34, Meeting of the Joint U.S. Section of the Combustion Institute, Washington, DC, March 15-17, 1999.
7. "An Augmented Reduced Mechanism for Methane Oxidation with Global Parametric and Detailed Structure Validation," by C. J. Sung, C. K. Law, and J.-Y. Chen, Paper No. 103, Meeting of the Joint U.S. Section of the Combustion Institute, Washington, DC, March 15-17, 1999.
8. "On Curvature-Affected Pulsating Instability in Inwardly-Propagating Spherical Flame," by C. J. Sung, C. J. Sun, and C. K. Law, Paper No. 204, Meeting of the Joint U.S. Section of the Combustion Institute, Washington, DC, March 15-17, 1999.
9. "Advances and Opportunities in Laminar Flames," by C. K. Law, Proc. of Second Asia-Pacific Conference on Combustion, Tainan, Taiwan, pp. 17-28, May 9-12, 1999.
10. "A Comprehensive Mechanism of C_2H_x and C_3H_x Fuel Combustion," by H. Wang, A. Laskin, Z. M. Djuriscic, C. K. Law, S. G. Davis, and D. L. Zhu, Paper No. 25, Fall Tech. Meeting of the Eastern States Section of the Combustion Institute, Raleigh, NC, Oct. 11-13, 1999.

11. "Pulsating Instability in Rich Hydrogen/Air Premixed Flames," by C. J. Sung and C. K. Law, AIAA Paper No. 2000-0577, 38th Aerospace Sciences Meeting, Reno, NV, January 10-13, 2000.
12. "On the Development of Detailed and Reduced Reaction Mechanisms for Combustion Modeling," by C. K. Law, C. J. Sung, and H. Wang, AIAA Paper No. 2000-0806, 38th Aerospace Sciences Meeting, Reno, NV, January 10-13, 2000.
13. "Modeling of Flame Dynamics in Complex Flows," by C. K. Law, Proceedings of the Third International Symposium on Scale Modeling, Nagoya, Japan, Sept. 10-13, 2000.
14. "Complex CSP for Chemistry Reduction and Analysis," by Tianfeng Lu, Yiguang Ju and C.K. Law, AIAA Paper No. 2001-0943, 39th Aerospace Sciences Meeting, Reno, NV, January 8-11, 2001.
15. "Determination of Laminar Flame Speeds Using Digital Particle Image Velocimetry," by T. Hirasawa, C.J. Sung, Z.W. Yang, H. Wang, and C.K. Law, Paper No. 138, 2nd Joint Meeting of the US Sections of the Combustion Institute, Oakland, CA, March 25-28, 2001.
16. "Effects of Aerodynamic Stretch and Curvature on Flame Pulsation," by C.J. Sung, A. Makino, and C.K. Law, Paper No. 262, 2nd Joint Meeting of the US Sections of the Combustion Institute, Oakland, CA, March 25-28, 2001.

PRESENTATIONS

Keynote and Named Lectures

1. "Advances and Opportunities in Laminar Flames," Second Asia-Pacific Conference on Combustion, Tainan, Taiwan, May 9-12, 1999. ****Keynote Lecture****
2. "Issues on Droplet Combustion and Gas-Phase Unsteadiness," Gordon Research Conference on Gravitational Effects in Physico-Chemical Systems, Henniker, NH, June 27 - July 2, 1999. ****Invited Lecture****
3. "Accomplishments and Challenges in Combustion Science," First International Conference on Engineering Thermophysics, Beijing, China, August 19-22, 1999. ****Invited Lecture****
4. "Modeling of Flame Dynamics in Complex Flows," Third International Symposium on Scale Modeling, Nagoya, Japan, Sept. 10-13, 2000. ****Invited Lecture****

5. "Frontiers of Combustion: From Microgravity to Microengines," College of Engineering, the University of Florida, Gainesville, FL, Oct. 19, 2000. ** Benton Lecture**
6. "The Role of Chemical Kinetics and Laminar Flames in the Modeling of Turbulent Flames," APS Division of Fluid Dynamics Conference, Washington, D.C., Nov. 19-21, 2000. **Invited Lecture**
7. "Advances and Needs in Flame Research," Second Joint US Sections Meeting of the Combustion Institute, Oakland, CA, March 26-28, 2001. **Invited Talk**
8. "Frontiers of Combustion: From Microgravity to Microengines," Tsinghua University, Beijing, China, April 23, 2001. **Inaugural Lecture as Guest Professor**
9. "The Role of Chemical Kinetics and Laminar Flames in Turbulent Flame Modeling," Technical Meeting of the Canadian Section of the Combustion Institute, Montreal, Canada, May 13-16, 2001. **Keynote Lecture**

Invited Departmental Seminars

1. "Dynamics of Droplet Collision, " Department of Mechanical Engineering, Stanford University, Palo Alto, CA, March 11, 1998.
2. "Kinetics and Transport in Nonpremixed Ignition of Hydrogen by Heated Air," Graduate Aeronautical Laboratories, Caltech, Pasadena, CA, March 13, 1998.
3. "Dynamics of Droplet Collision," Department of Mechanical Engineering, Case Western Reserve University, Cleveland, OH, April 10, 1998.
4. "Aerodynamics of Laminar Flames," Department of Mechanical and Aerospace Engineering, Arizona State University, Tempe, AZ, February 12, 1999.
5. "Advances and Opportunities in Laminar Flames," National Heat Transfer Conference, Albuquerque, NM, August 15-17, 1999.
6. "Dynamics of Droplet Collision," Department of Chemical Engineering, University of Illinois, Chicago, IL, January 27, 2000.
7. "Some Aspects of the Ignition-Extinction S-Curves in Combustion Phenomena," Department of Theoretical and Applied Mechanics, University of Illinois at Urbana-Champaign, IL, Oct. 12, 2000.
8. "Aerodynamics and Chemistry in Flame Propagation and Modeling," Department of Mechanical Engineering, University of Pennsylvania, Philadelphia, PA, April 5, 2001.
9. "Aerodynamics of Flames," Department of Engineering Mechanics, Tsinghua University, Beijing, China, April 24, 2001.

10. "The Role of Chemistry in Flames," Department of Thermal Engineering, Tsinghua University, Beijing, China, April 25, 2001.

Contributed Talks

1. "The Role of Hydrodynamic Instability in Flame/Vortex Interaction," 34th AIAA Joint Propulsion Conference, Cleveland, OH, July 12-15, 1998.
2. "Steady and Pulsating Propagation and Extinction of Rich Hydrogen/Air Flames at Elevated Pressures," 37th Aerospace Sciences Meeting, Reno, NV, January 11-14, 1999.
3. "Hydrodynamic Instability in Flame-Vortex Interaction," National Heat Transfer Conference, Albuquerque, NM, August 15-17, 1999.
4. "On the Establishment of Stationary Flame Balls," Fall Tech. Meeting of the Eastern States Section of the Combustion Institute, Raleigh, NC, Oct. 11-13, 1999.
5. "Pulsating Instability in Rich Hydrogen/Air Premixed Flames," 38th Aerospace Sciences Meeting, Reno, NV, Jan. 10-13, 2000.
6. "On the Development of Detailed and Reduced Reaction Mechanisms for Combustion Modeling," 28th Aerospace Sciences Meeting, Reno, NV, Jan. 10-13, 2000.
7. "Dynamics and Extinction of Non-Adiabatic Particle-Laden Flames," 28th International Combustion Symposium, Edinburgh, Scotland, July 30-August 4, 2000.
8. "Studies of Spray Detonation for PDE Applications," 39th AIAA Aerospace Sciences Meeting, Reno, NV, Jan. 8-11, 2001.

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T. F. Lu (Ph. D. Candidate)

C.J. Sun (Ph. D., 1998)

J. Yuan (Ph. D. Candidate)